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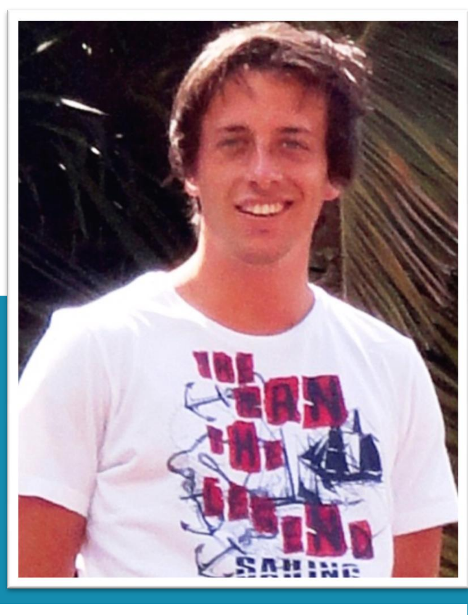
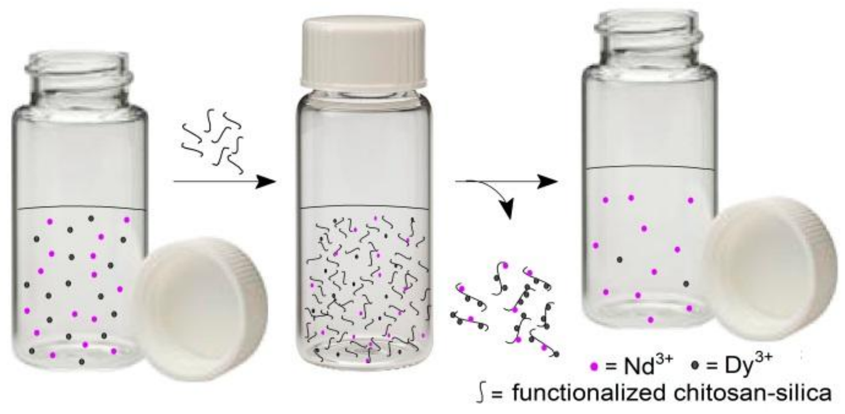


Adsorption Performance of Functionalized Chitosan-Silica Hybrids towards Rare Earths



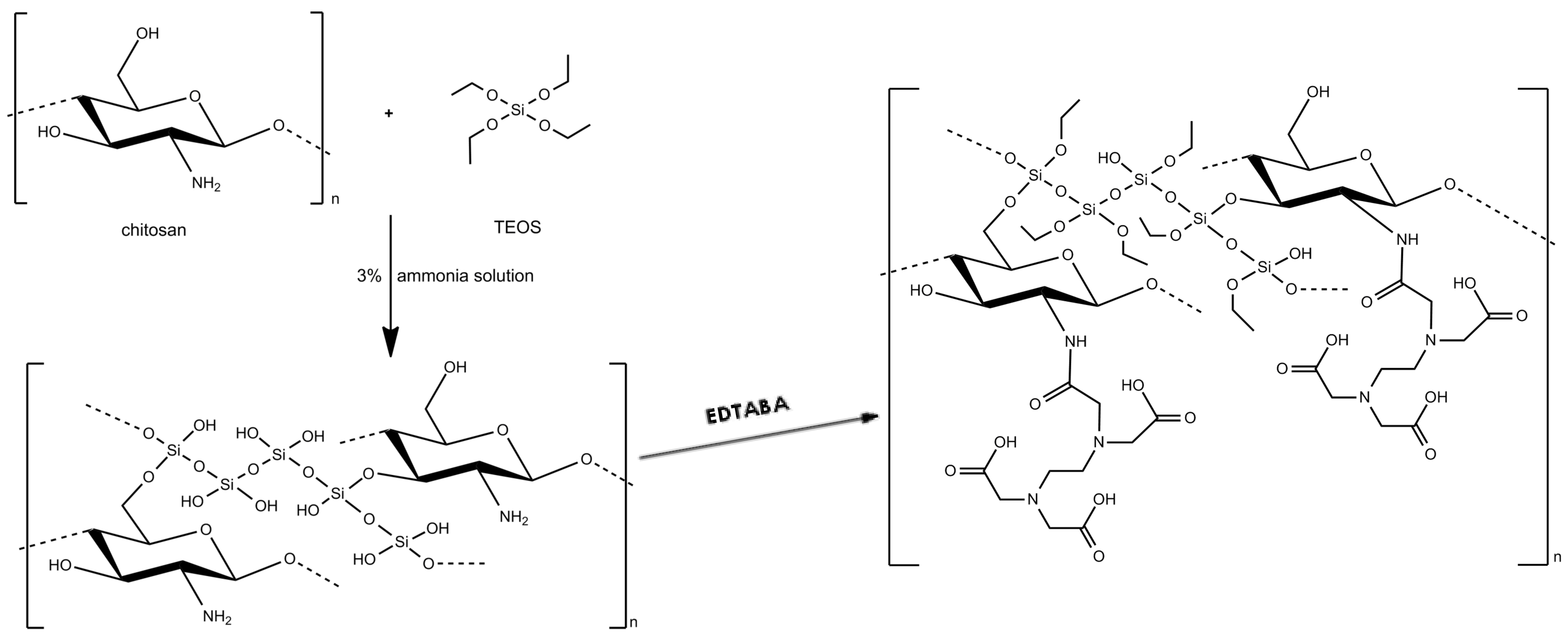
Objectives

- *Synthesis of functionalized chitosan-silica particles*
- *Adsorption studies with Nd(III) as a function of several parameters, like adsorbent mass, aqueous pH and adsorption cycle*
- *Investigation of selectivity amongst rare-earth ions*

Background

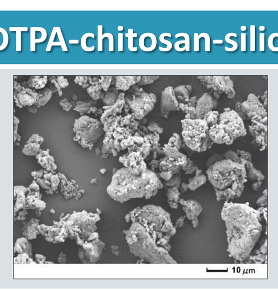
In our evolution towards a more sustainable society, biosorption offers advantages due to the cost-effective, environmentally friendly and virtually unlimited supply of bioresources. One of the most promising biosorbents is chitosan, a linear polysaccharide composed of β-(1,4)-linked D-glucosamine moieties. Besides its non-toxicity, bio-degradability and reusability, chitosan is specifically advantageous because it contains a high concentration of amino groups, which are easy to functionalize. This results in a high adsorption capacity and selectivity for metal ions. Therefore, chitosan could find application in the recovery of rare earths from diluted waste streams, like industrial slags. These rare earths could then be mutually separated by means of ion-exchange column chromatography with functionalized chitosan-silica as packing material.

Synthesis



To increase the porosity and rigidity of chitosan, it was hybridized with silica in a sol-gel reaction. The resulting material was then functionalized with EDTA and DTPA in order to improve the adsorption capacity of and selectivity for and amongst rare-earth ions.

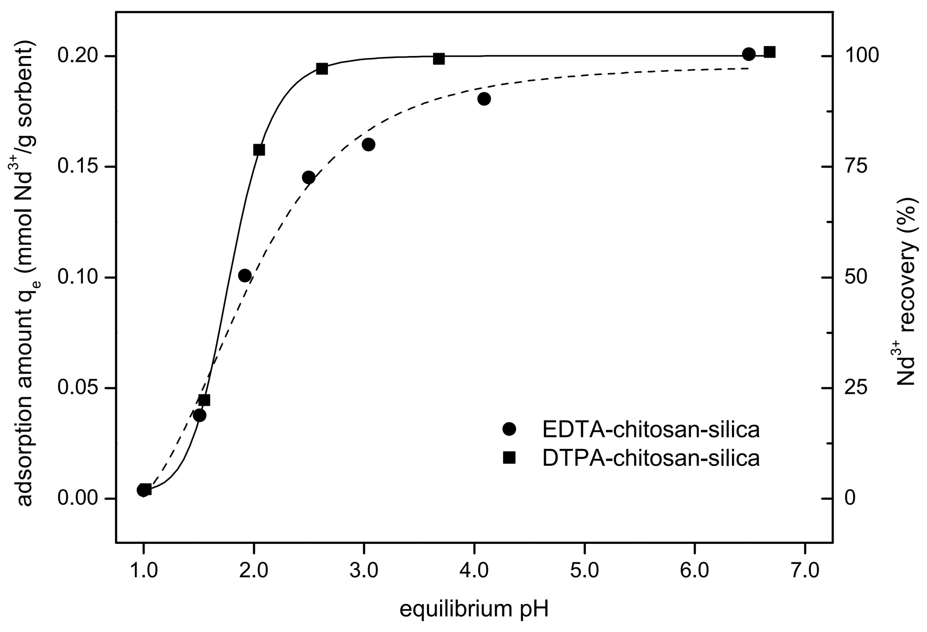
Characterization

Chitosan	Chitosan-silica	EDTA-chitosan-silica	DTPA-chitosan-silica
			
SSA = 1 m²/g	SSA = 219 m²/g	SSA = 230 m²/g	SSA = 198 m²/g
TPV = 0.003 cm³/g	TPV = 1.030 cm³/g	TPV = 1.030 cm³/g	TPV = 0.573 cm³/g
Organic content	25.8%	31.0 % organic	29.7% organic
Organic : Inorganic	1 : 3 / 1 : 3	3 : 7	3 : 7

SSA = specific surface area; TPV = total pore volume (both obtained from N_2 sorption)

The reported ratios of organic (chitosan) and inorganic (silica) material in the chitosan-silica hybrid particles are average values resulting from three distinct analysis techniques: TGA, ICP and CHN.

Influence of aqueous pH



Adsorption increases sigmoidally with pH with maximum adsorption from pH 4 on.

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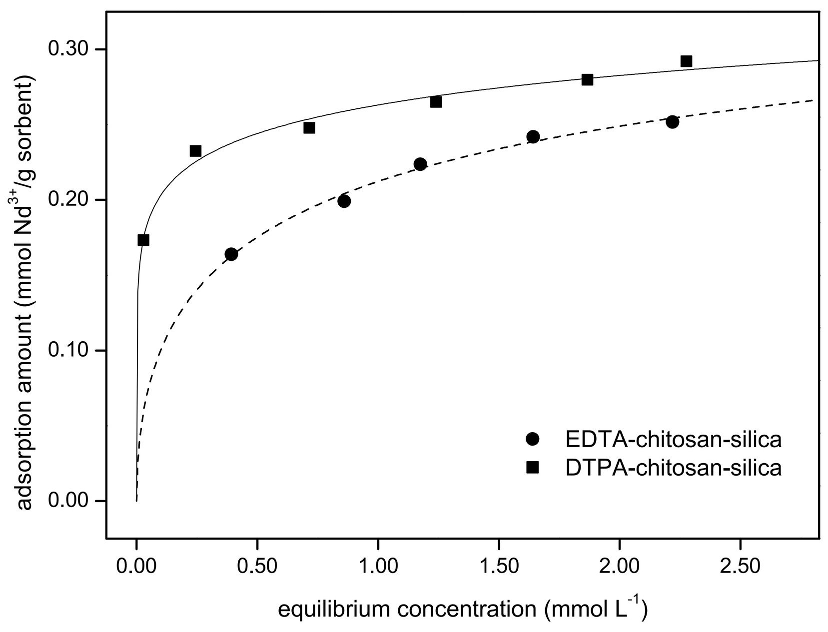
$C_{aq}(Nd^{3+})$ = 0.51 mmol/L
Adsorbent mass = 25.0 mg
Contact time = 4 hr
Temperature = RT

Influence of adsorbent mass



The adsorption capacity for DTPA-CS is higher than for EDTA-CS.

Data was fitted with the Langmuir-Freundlich model.

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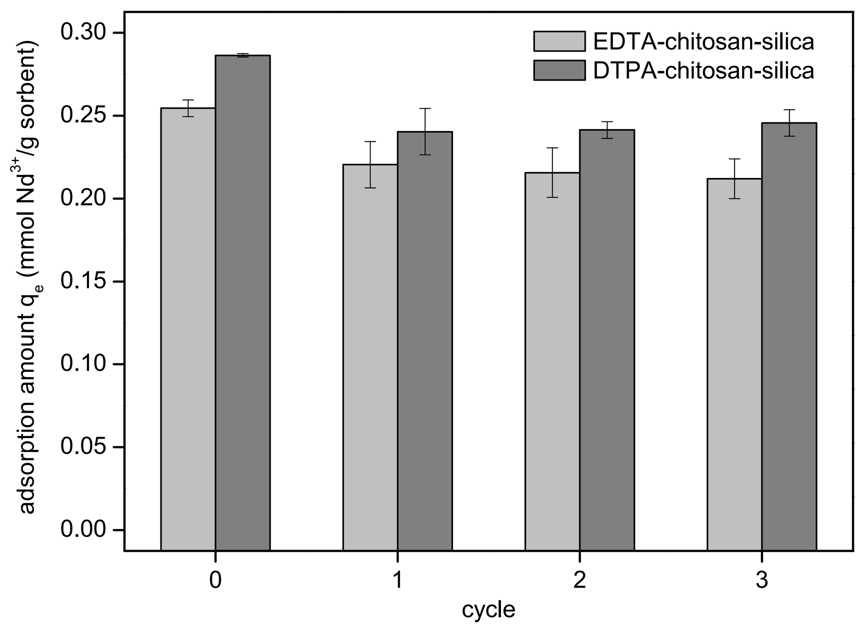
$C_{aq}(Nd^{3+})$ = 2.57 mmol/L
Contact time = 4 hr
Temperature = RT

Investigation of reusability



Adsorption efficiency remains constant after initial drop (of about 20%) after first stripping cycle.

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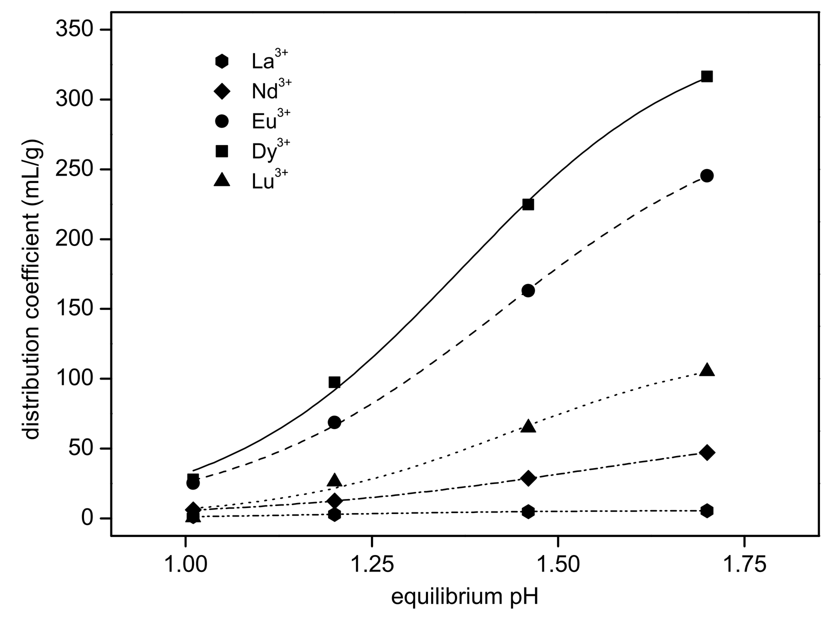
$C_{aq}(Nd^{3+})$ = 1.05 mmol/L
Contact time = 4 hr
Stripping occurred by shaking the loaded particles with HCl (1.0 M) for 5'

Investigation of selectivity amongst rare earths

Selectivity was investigated for DTPA-chitosan-silica in an aqueous mixture of La(III), Nd(III), Eu(III), Dy(III) and Lu(III).



Differences in affinity for DTPA-chitosan-silica are observed between the lanthanide ions as a result of differences in the corresponding stability constants.

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$C_{aq}(Ln^{3+})$ = 0.75 mmol/L
Contact time = 4 hr

Conclusions

- By hybridization, the resulting adsorbents (composed of 30% functionalized chitosan and 70% silica) combine the advantages of both components: the high adsorption capacity and selectivity of chitosan and the rigidity and porosity of silica.
- The adsorption performance and reusability of the functionalized materials were investigated with Nd^{3+} as a model system for all rare earths.
- A high selectivity amongst different rare-earth ions was observed in for DTPA-chitosan-silica a multi-element solution of several lanthanide ions.
- Future work will consist of using the functionalized chitosan-silica as resin material in order to separate rare earths by column chromatography.

Publication: J. Roosen, K. Binnemans, *Adsorption and chromatographic separation of rare earths with EDTA- and DTPA-functionalized chitosan biopolymers*, Journal of Materials Chemistry A, 2, 1530–1540 (2014)